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## SIZE EFFECTS AND EMBEDDING IN CLUSTER MODELS FOR HYDROGEN CHEMISORPTION

A. VAN DER AVOIRD, H. DE GRAAF and R. BERNIS

*Institute of Theoretical Chemistry, University of Nijmegen, Nijmegen, The Netherlands*

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In a self-consistent calculation of hydrogen chemisorption on "cubium" clusters of various size we have found that by chemisorption localized bonds (surface molecules) can be formed, even on broad band metals. The cluster size required for chemisorption studies is considerably less than for describing the metallic properties. Theoretical models for embedding clusters in an underlying solid should take electron repulsion terms into account to the same level of approximation in the clusters as in the solid, since otherwise instabilities may result from a different screening.

## 1. Introduction

For the theoretical study of chemisorption of (single) atoms or molecules on metal or semiconductor surfaces two types of models are commonly used<sup>†</sup>: cluster models and semi-infinite crystal models. Although the latter models may seem more attractive at first sight, in practice rather strong simplifications must be made in the description of the semi-infinite solid. Either one uses the jellium model [2,3], in which case one has to reintroduce the atomic character of the solid in some approximate way [4], or one applies semi-infinite crystal treatments which are actually (small) cluster calculations where the cluster is embedded in the solid in some approximate manner. In its simplest form this embedding means that the solid (metal) is considered as a reservoir of electrons which are flowing into and out of the cluster. This flow is directed by the relative Fermi energies of the cluster and the solid together with the electron repulsion in the adatom (Anderson's model) [5] or also in the metal atoms (Hubbard's model) [6]. A more advanced technique of embedding using a Dyson resolvent equation is proposed by Grimley and Pisani [7] who treat a cluster AB, where A is the adsorbed (hydrogen) atom and B is a metal ("cubium") atom, interacting with the underlying ("cubium") solid. Whereas the

electron repulsion effects in the cluster AB are explicitly included and this cluster is treated self-consistently the underlying solid is described in a tight-binding (Hückel) model, however.

These examples illustrate that not only the cluster model is an approximate one, because of its limited number of atoms, but that also the semi-infinite crystal models contain various simplifications. Therefore, it is important to consider a number of questions. When using the cluster model one must know what the cluster size should be in order to describe the chemisorption effects correctly, i.e. how localized are these effects? Is it necessary that the clusters accurately reflect the properties of the solid (band structure, cohesion energy, etc.) or is this too strong a requirement for chemisorption clusters? When embedding the cluster which contains explicitly the electron repulsion terms, in a tight-binding solid where these terms are not considered [7], one may ask whether this form of embedding is effective and whether it does not lead to artefacts. An interesting study of the latter problems is made by Grimley and Mola [8] who use the embedding model of Grimley and Pisani [7] for clusters AB embedded in larger finite clusters  $M_n$  (cubium,  $n \leq 152$ ) and compare the results with other approximate models where electron repulsion is taken into account and self-consistency is extended over the whole cluster  $ABM_n$ . So they have performed calculations on cubium with a Hartree-Fock Hubbard model

<sup>†</sup> A recent literature review is given in ref. [1].



for  $n \leq 13$  and on lithium with a CNDO method for  $n \leq 22$ .

The best check on the embedding methods as proposed by Grimley and Pisani, however, is to perform a full LCAO SCF calculation on the large clusters treated by Grimley and Mola, including electron repulsion and overlap which in the Grimley–Pisani model are restricted to the AB cluster only. We have performed calculations for hydrogen chemisorption on cubium clusters ( $n \leq 39$ ), compared our results with those of Grimley and Mola and, at the same time, studied the effects of cluster size in a fully self-consistent model including electron repulsion and overlap.

## 2. Calculations

Although cubium is only a hypothetical metal, it has nevertheless been studied intensively, particularly in connection with the problem of adsorption [7–14]. Our calculations were performed for a hydrogen atom adsorbed on top of a cubium atom at the (100) surface, where the cubium is represented by hemispherical clusters of increasing size ( $1 \leq n \leq 39$ ). These clusters were obtained by adding successively the first (b), second (c), etc., shells of neighbours to the central cubium atom  $M_a$  (fig. 1). Just as Grimley et al. [7,8] and Paulson and Schrieffer [11] we have represented the hydrogen atom and each cubium atom by a single *ls*-type gaussian orbital (GTO) and let each atom contribute one electron to the system. The exponent for the hydrogen GTO is the energy optimized atomic value ( $\alpha_H = 0.28 \text{ bohr}^{-2}$ ,  $\epsilon_H = -0.42 \text{ hartree}$ );

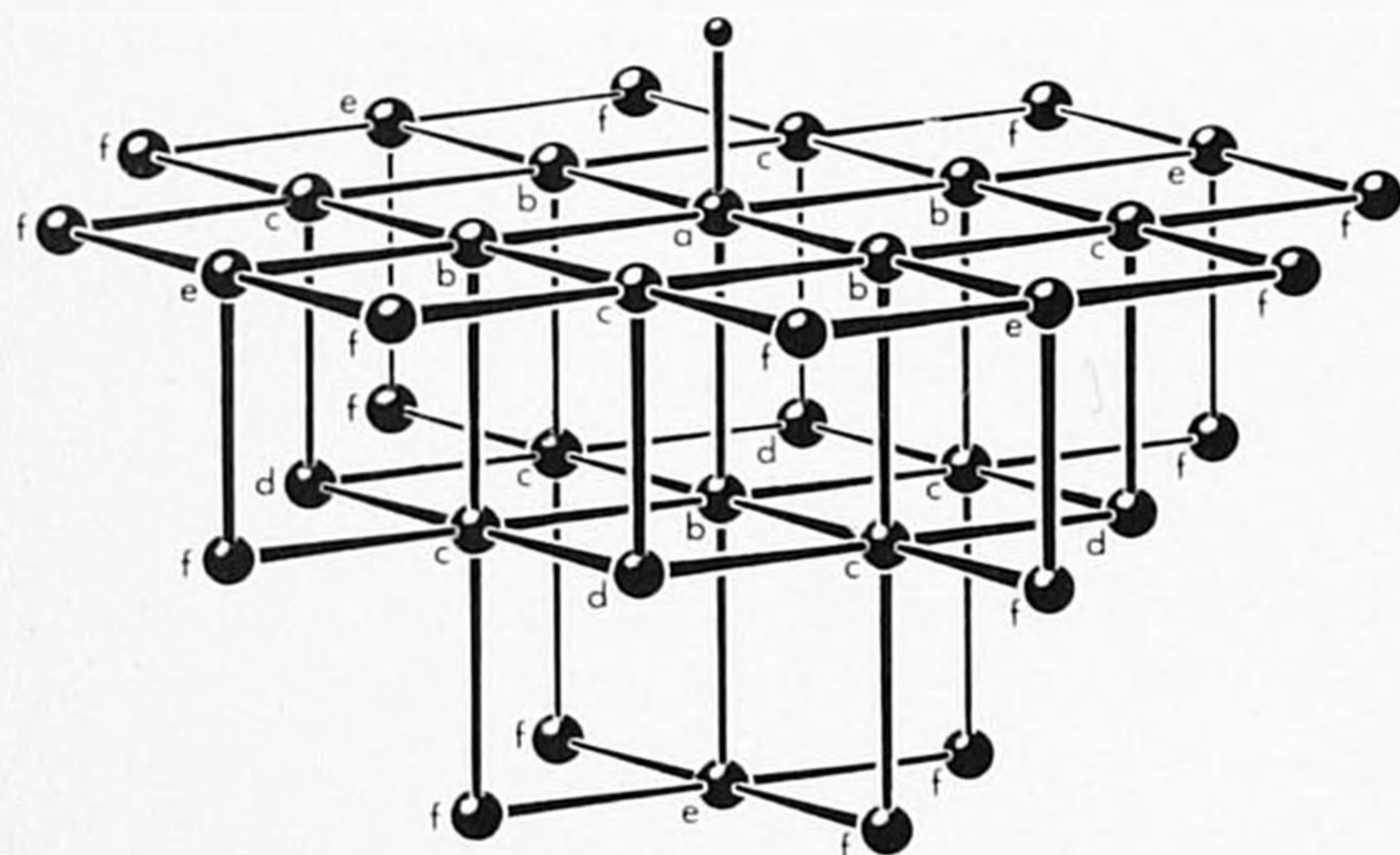


Fig. 1. Model clusters for hydrogen chemisorption on a cubium (100) surface.

the cubium exponent has been taken from refs. [7,11] as  $\alpha_M = 0.07 \text{ bohr}^{-2}$  ( $\epsilon_M = -0.32 \text{ hartree}$ ) which, in combination with a lattice constant of 4.75 bohr, yields a rather broad band (about 15 eV [11]). As we shall see, this parameter choice yields the most interesting results among the different (smaller) band widths considered by Grimley et al. [8] and by Paulson and Schrieffer [11].

For each of the clusters  $M_n$  and  $HM_n$  with  $n = 1, 6, 14, 18, 23, 39$ , we have performed LCAO SCF calculations by the restricted Hartree–Fock scheme both for closed and open shell systems [15,16]. We have used the integral program of IBMOL-6 [17], coupled via a symmetry transformation program [18] to the closed and open shell SCF program of Bagus [19]. Since, for the larger clusters, many open and closed shell orbital energies lie very close to each other we have always calculated many different (singlet, doublet and triplet) states arising from various electron configurations and selected the state with the lowest total energy. Because states of the same symmetry are lying close also, the calculation could certainly have been improved by using configuration interaction or multi-configuration SCF procedures, but we have not tried this, as our main goal was to compare the results with those of other SCF models.

## 3. Results and discussion

From the results on the isolated cubium clusters,  $M_n$ , which are summarized in table 1, we observe that the metal properties begin to converge for the largest clusters considered. Because the number of nearest neighbour bonds per atom is still rather low relative to the bulk value (3 bonds/atom) or the value for an ideal surface atom (2.5 bonds/atom), we expect a further gradual change in the properties for  $n \rightarrow \infty$ . For the same parameter choice Paulson and Schrieffer [11] estimated a nearest neighbour hopping matrix element  $T = -0.046 \text{ hartree}$  and a corresponding bulk band width  $W = 0.55 \text{ hartree} = 14.9 \text{ eV}$  in the tight-binding model ( $W = 12|T|$ ). From our calculations it appears that this nearest neighbour Fock matrix element is about  $-0.19 \text{ hartree}$ , but also that the next nearest neighbour element equals  $-0.11 \text{ hartree}$  and that the corresponding overlap matrix elements are 0.45 and



Table 1  
Results for cubium clusters  $M_n$

$n$	Number of nearest neighbour bonds per atom	Band width (hartree)	Cohesion energy per atom (hartree)	Cohesion energy per nearest neighbour bond (hartree)	Fermi level a) (hartree)
1	0.00	0.00	0.0000	0.0000	-0.32
6	0.83	0.20	-0.0116	-0.0139	-0.20 (-0.29)
14	1.50	0.49	0.0068	0.0045	-0.24
18	1.83	0.55	0.0126	0.0069	-0.27
23	1.65	0.55	0.0087	0.0053	-0.22 (-0.30)
39	1.79	0.56	0.0119	0.0067	-0.21 (-0.23)

a) The energy of the highest occupied MO. When a lower lying open shell is present, its energy is added in parentheses.

0.20, respectively. Therefore, the assumptions of the simple tight-binding model are certainly not valid.

For the smaller clusters, in particular, we would probably have found a larger cohesion energy if we had optimized the lattice constant. The optimum value of the lattice constant increases in going from the diatomic  $M_2$  molecule to the larger clusters; we have kept the same lattice constant for all clusters, however, just as was done in refs. [7,8,11].

After adsorbing a hydrogen atom on these clusters and optimizing its height such that the maximum adsorption energy is obtained, we observe some characteristic features in the MO level diagram\* and in the gross atomic orbital populations [20] per energy level (see fig. 2, for  $n = 39$ ), which can be compared with the total and the local density of states, respectively, for the semi-infinite crystal. Such features have been studied qualitatively, as a function of the parameters in tight-binding Hückel models, for adsorption on semi-infinite cubium [9,10,13]. From the energy level diagram (the total density of states) it looks as if the rather diffuse band of the metal cluster,  $M_{39}$ , splits off one level at the bottom and one at the top as a result of the interaction with the discrete H-atom level (which is lying rather low in the band).

\* The band gap of about 0.1 hartree which is observed in this level diagram just above the Fermi level is an artefact of the Hartree-Fock method; it arises because the Fock operator for the occupied orbitals contains an  $(N-1)$ -electron potential, whereas the operator for the virtual orbitals contains an  $N$ -electron potential [21].

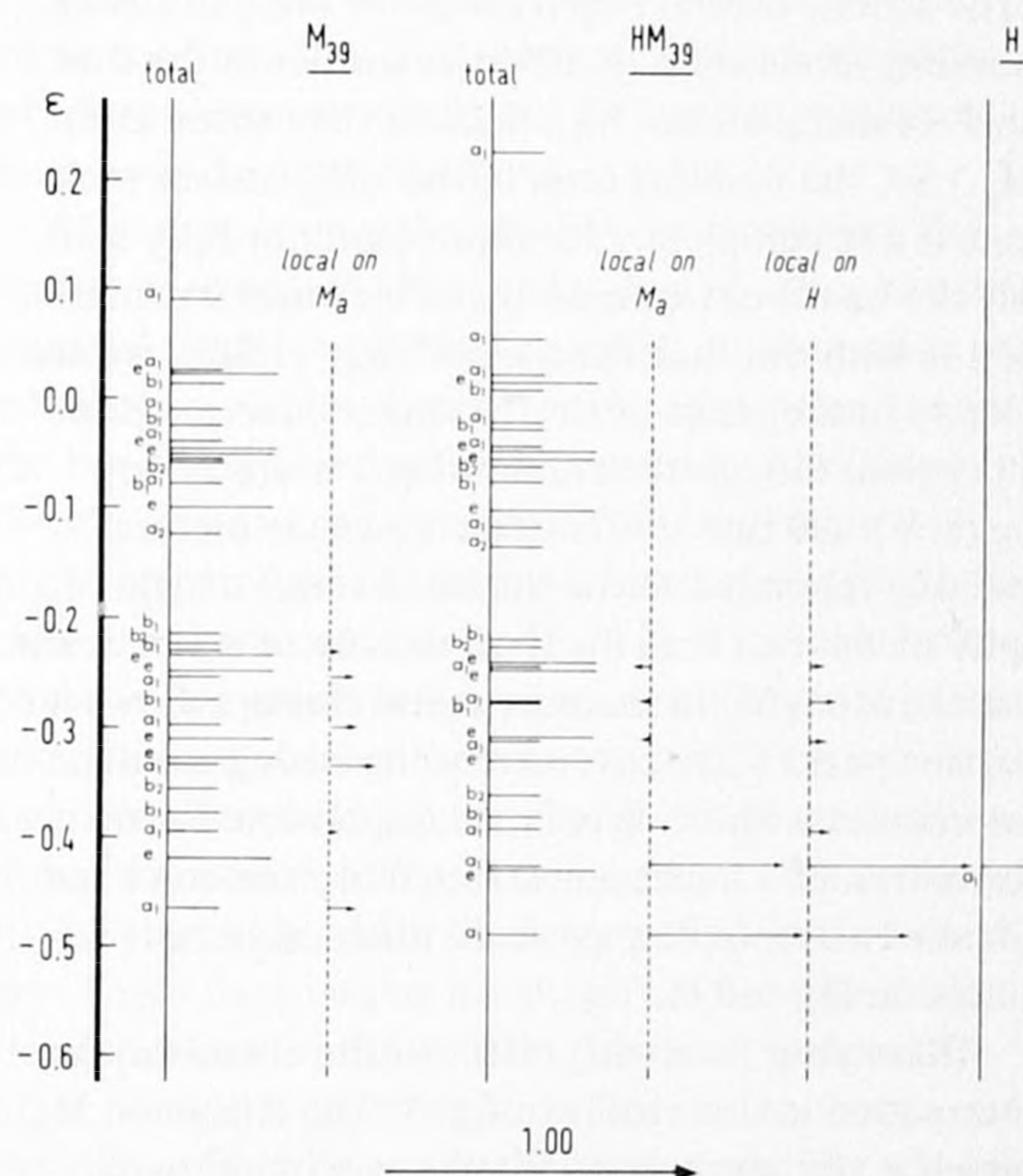


Fig. 2. Effect of hydrogen chemisorption on the MO level diagram (total density of states) and some gross atomic populations per energy level (local densities of states) of a 39-atom cubium cluster. The orbitals are classified with respect to the irreducible representations of the symmetry group  $C_{4v}$ . The atomic populations are only shown for the occupied levels. The arrow at the bottom corresponds with an atomic population equal to 1.00.

These "split-off" levels point to a strong bonding/anti-bonding interaction between the H atom and the



cluster. (The Fock matrix element between H and the central atom  $M_a$  equals  $-0.35$  hartree, the overlap is  $0.56$ , which is to be compared with a nearest neighbour Fock matrix element of  $-0.19$  hartree and a nearest neighbour overlap of  $0.45$  in the metal.)

Looking at the atomic orbital populations (the local density of states) on  $M_a$  and on H, which are plotted in fig. 2 for the occupied levels, the occurrence of these strong adsorption interactions is confirmed: the local density of states on  $M_a$  is very diffuse in the pure metal clusters; upon H adsorption it forms very pronounced peaks at the bottom of the band  $\ddagger$  corresponding to localized covalent bonding in the "surface molecule"  $HM_a$  (at the cost of the density of states in the center of the band). We do not find just one split-off peak below the band, however, but two strong bonding peaks and a weaker third one. (The atomic orbital populations for the two strong bonding levels are 5 to 10 times smaller in the first shell of metal atoms,  $M_b$ , than on the central atom  $M_a$ .) So, the bonding level in the  $HM_a$  surface molecule is not completely localized (and not fully split off the band) but is somewhat broadened by interaction with the "indented solid"  $M_{n-1}$ . Still, we are clearly in the range of the "strong interaction limit" [11] even though the cubium band width is very large. We see that the "surface molecule picture" (weakly rebonded to the indented solid) is valid in spite of the fact that the local density of states at the surface atom  $M_a$  in the pure metal clusters shows no narrow peaks [22–24]; merely the strong covalent interaction with the H atom is responsible for the formation of a localized surface molecule bond and for the corresponding peaks in the local density of states on  $M_a$  and H.

This strong localizing effect of the chemisorption interaction is also visible in fig. 3. The charge on  $M_a$  which is still strongly oscillating as a function of cluster size in the pure metal clusters, is stabilized by the interaction with H. Also, fig. 4 shows the effect of a localized H– $M_a$  bond: when the H–M distance is varied, the H– $M_a$  molecule as a whole remains almost neutral (it is covalent at the equilibrium distance) and the surrounding M atoms are only slightly affected.

From fig. 5 we observe that for the adsorption energy the recoupling of the surface molecule to the in-

$\ddagger$  Also at the top, but these are not shown in fig. 2.

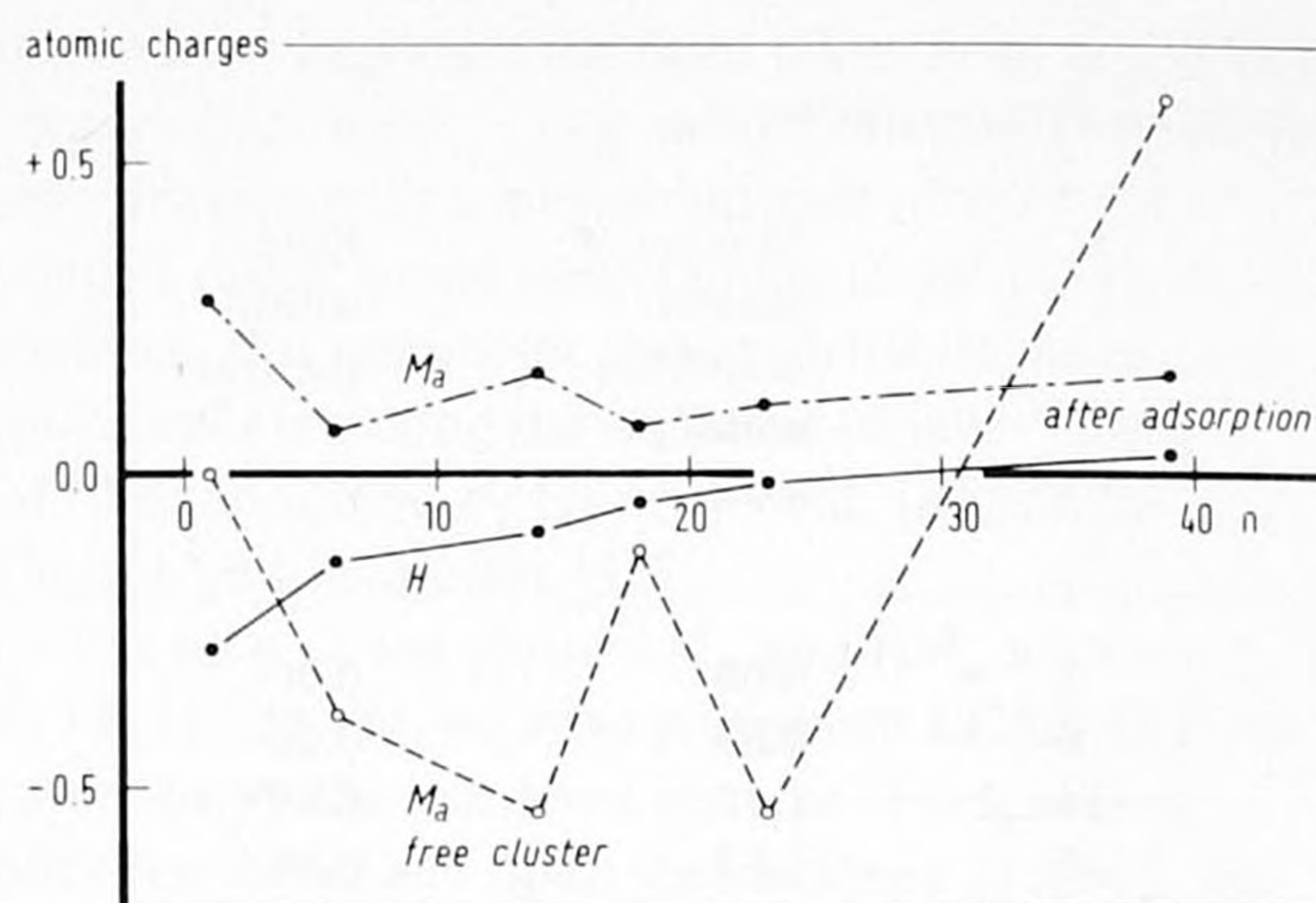


Fig. 3. Some atomic charges in cubium clusters of various size, before and after hydrogen chemisorption.

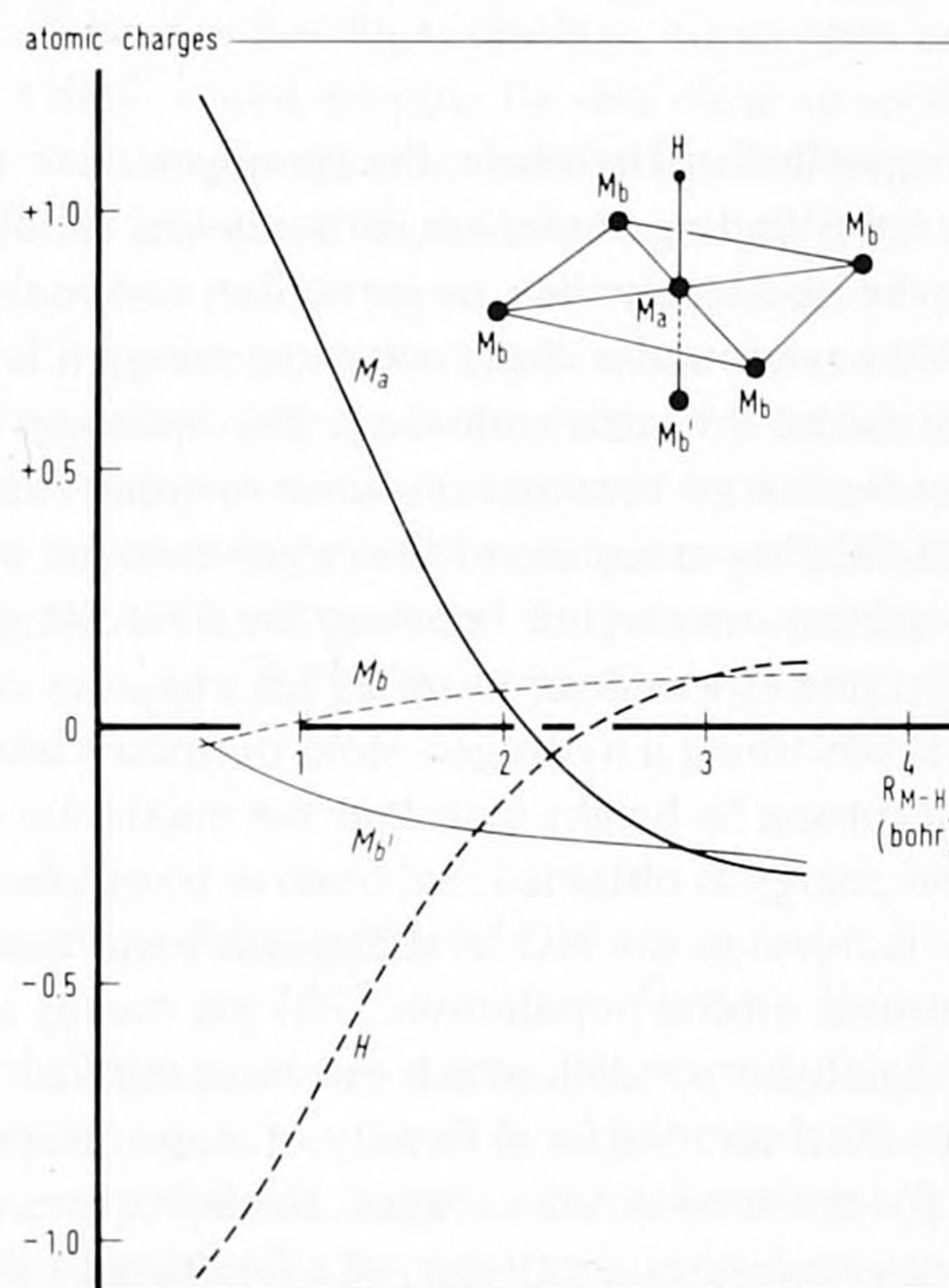


Fig. 4. Effect of variation in H–M distance on the atomic charges in a  $HM_6$  cluster.

dent cluster is very important: the binding of H–M ( $\Delta E = 65$  kcal/mole) is considerably weakened (to about 30 kcal/mole) by this recoupling. One shell of cubium neighbours ( $HM_6$ ) is already sufficient to cause this weakening, though, to a value which does not deviate much anymore from the values for larger clusters. It is typical that in the fluctuations of  $\Delta E$  with cluster size the smallest (absolute) values of  $\Delta E$  are found for those metal clusters which are relatively stable and compact, for instance  $M_{18}$  (see table 1).



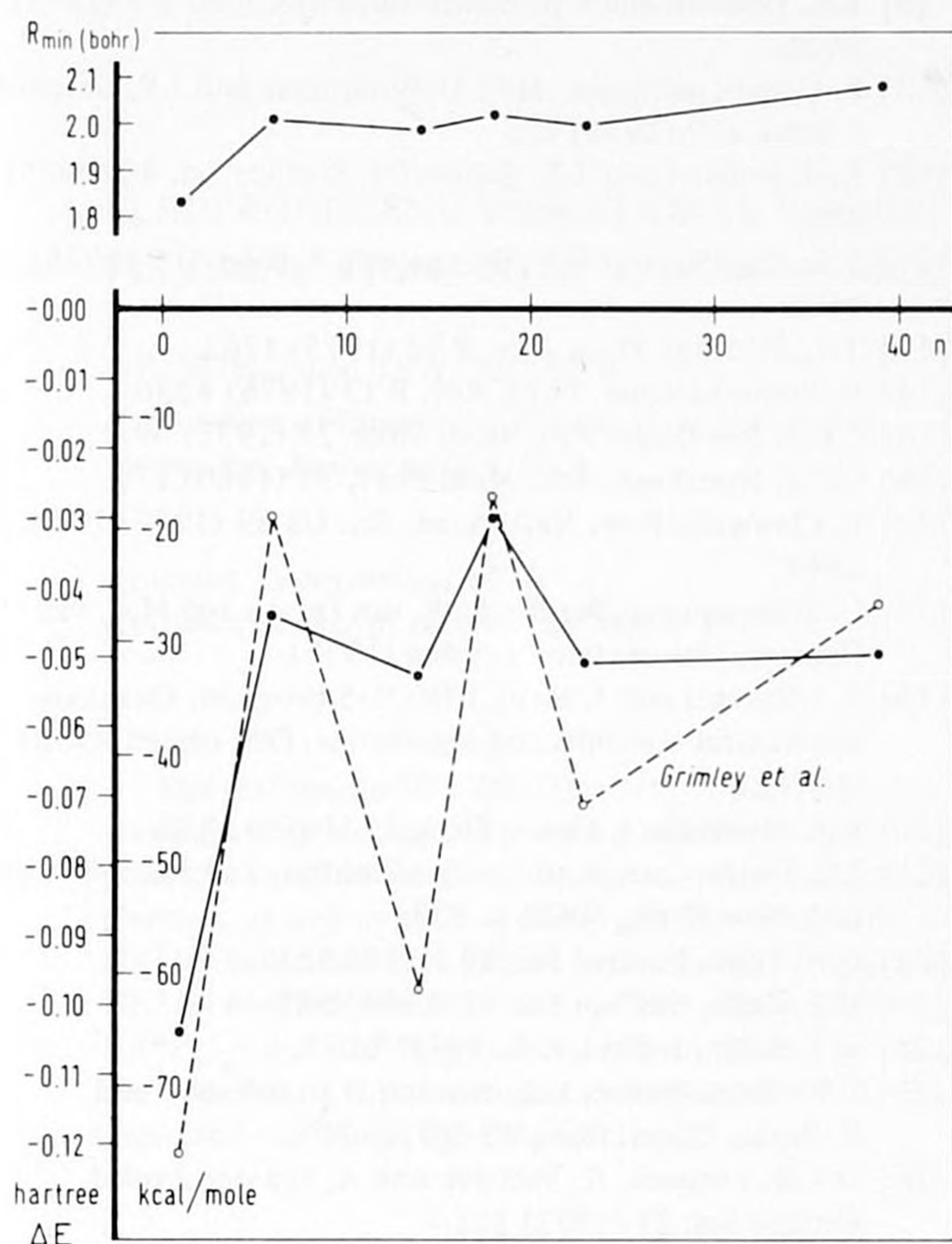


Fig. 5. Adsorption energy,  $\Delta E$ , and equilibrium height,  $R_{\min}$ , for hydrogen chemisorption on cubium clusters of various size. The dashed line shows the corresponding results for  $\Delta E$  calculated with the embedding model of Grimley and Pisani [7] and Grimley and Mola [8] (for  $\beta = 0.046$ , cubium band width 0.55 hartree).

The same phenomenon has been observed by Bauschlicher et al. [25] in their calculations on  $HBe_n$  clusters, although their clusters are smaller and their fluctuations in  $\Delta E$  are more pronounced.

In fig. 5 we have also plotted the fluctuations in the adsorption energy calculated by Grimley and Mola [8] using the Grimley–Pisani model [7] for embedding the surface molecule  $HM_a$  in the clusters  $M_n$ . It is clear that this approximate method of embedding yields considerably larger fluctuations in  $\Delta E$  so that much larger clusters would be required before the adsorption energy converges.

#### 4. Conclusions

It is rather striking that even for metal clusters

having a broad band (15 eV wide) the interaction with hydrogen atoms, leading to an adsorption energy of about 1 eV only, can cause strong localization of the bonding electrons resulting in a “surface molecule”. This surface molecule is formed by the adsorption itself and does not require the presence of localized electrons (narrow peaks in the local density of states) at the pure metal surface [22–24]. This means, for instance for transition-metals, that also the conduction electrons (4s, 4p in the first row and not just the narrow-band 3d electrons) can take part in the covalent bonding with adsorbed hydrogen. We have stressed this point already on the basis of earlier calculations for hydrogen adsorption on nickel clusters [26,27] or periodic nickel films [28]. Since these calculations have used the extended Hückel method in which the bonding is heavily determined by overlap criteria, we think that our present result is a worthwhile confirmation, as it originates from a model in which the electron repulsions are explicitly taken into account in a self-consistent manner.

The second conclusion is that for recoupling the surface molecule  $H-M$  to the indented solid, one shell of metal neighbours, forming a  $HM_6$  cluster, gives very satisfactory results already for the adsorption energy, the bond length and related quantities (vibrational force constants, for instance). This conclusion will hold even stronger for narrower band metals (the other parameters studied in refs. [8,11]). The calculation of the metal properties requires much larger clusters and, also, we observe that for the largest clusters we have considered ( $M_{39}$ ) the charge distribution still shows considerable fluctuations, even in the center of the cluster, when extra shells are added at the boundary. These fluctuations hardly affect the chemisorption behaviour of the clusters, however, and, on the other hand, the chemisorption interaction damps out the charge fluctuations in the cluster near the adsorption site. So, rather small clusters are satisfactory for chemisorption studies, even if no embedding is considered. As a rule of thumb one could prescribe that any surface atom directly “contacting” the adsorbed atom should possess its complete shell of nearest neighbours. This same conclusion we have drawn already from the extended Hückel calculations [26–28] but, again, it is important to note that it holds also in a model where the (long range) electrostatic effects are explicitly induced.



Finally, we remark, in agreement with the conclusion made by Grimley and Mola on the basis of more approximate calculations [8], that the embedding of a cluster is most effective when the surrounding crystal (or larger cluster) is treated in the same model. If we include electron repulsions near the adsorption site but not in the surrounding cluster, fluctuations may arise due to the lack of screening and the results may become unstable with respect to cluster size.

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